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PROVISIONAL SPECIFICATION

FOR THE INVENTION ENTITLED:

"PROCESS AND DEVICE FOR PRODUCTION OF LNG BY REMOVAL OF FREEZABLE SOLIDS"

The invention is described in the following statement:-

Process and Device for Production of LNG by Removal of Freezable Solids

Field of the Invention

The present invention relates to a process and device for the production of pressurised liquid natural gas by removing a range of freezable species such as carbon dioxide, water and heavy hydrocarbons as part of the cryogenic process of liquefying natural gas.

Background of the Invention

Natural gas can contain a wide range of compositions of species which are capable of forming solids during the cryogenic process of liquefying natural gas. Such species are known as "freezable". In a conventional LNG facility, pretreatment of the natural gas is required to remove these freezable species prior to the liquefaction stage. Depending on the feed gas composition, pressure and temperature, these components are usually removed by various methods depending on the particular species involved. On average, CO_2 compositions in a natural gas feed stream can range between 0.5% and 30% and could be as high as 70% in still commercially viable reservoirs like Natuna. Also, natural gas is normally saturated with water and heavy hydrocarbons unless these have been reduced to meet pipeline dew point specifications.

In a typical LNG facility, CO_2 is normally removed down to 50-125ppm and H_2S down to 3.5 mg/Nm^3 prior to the natural gas entering a liquefaction process. These components are typically removed by chemical reaction in a reversible absorption process using an amine solvent. This is an expensive and complex process and commonly encounters operational problems such as foaming, corrosion, blocked filters, amine degradation, and losses of amine, water and hydrocarbons. The process also consumes energy to regenerate and pump the solvent.

Treated gas from the amine system will be water saturated and needs to be dried to less than 1ppm prior to liquefaction. This is normally achieved by using fixed-bed solid adsorbents such as molecular sieves. Other dehydration processes such as glycol, methanol or membranes do not achieve the low dew point required for cryogenic liquefaction.

The natural gas feed stream is sometimes pretreated to partially remove water along with some heavy hydrocarbons by means of a pre-cooling cycle from the main refrigeration unit. Alternatively, Joule-Thomson cooling can be used if excess feed gas pressure is available. Care must however be taken to keep the gas above the hydrate formation temperature.

This is again a relatively expensive process. Large insulated pressure vessels are required along with a regeneration system. Regeneration of the molecular sieve is required and this consumes energy to heat the gas. The regen gas must be heated prior to entering the "wet" adsorption unit, then cooled to remove water before it is recycled (usually compressed) to the inlet of the duty adsorption unit. If a molecular sieve is used to remove CO_2, the regeneration gas must be disposed of or used as fuel gas.

Heavy hydrocarbons (typically C_6+) must be removed to a level where they will not freeze in the heat exchangers. The components can be partially removed along with water as explained above. Where further removal is required, a cryogenic distillation column is required, with cooling provided from the main refrigerant cycle. Again, this can be an expensive and complex process, especially if the removed components are required for refrigerant make-up in a mixed refrigerant cycle.

In conventional LNG plants, heat transfer for cooling a natural gas feed stream sufficiently to form a liquid is effected in a heat exchanger. Freezable species which are not removed prior to entering the cryogenic LNG cooling vessel precipitate and accumulate on the cold surfaces of the heat exchangers and other equipment, eventually rendering these items inoperable. When fouling has reached a sufficient level, the vessel must be taken off-line for the fouling to be removed. In the process the vessel, baffles or pipework can be damaged which only encourages further fouling in the next production cycle. Moreover, solids condensing on metal surfaces form an insulating film reducing thermal efficiency of the heat exchanger.

There is a need for a simpler, more economical process for production of LNG by removing freezable species from natural gas feed streams as an integral part of the liquefaction process to overcome the problems associated with fouling of plant equipment. An aim of the present invention is to eliminate the expensive and complex pretreatment processes of the prior art described above.

Summary of the Invention

According to one aspect of the present invention there is provided a process for the production of pressurised LNG from a natural gas feed stream containing at least one freezable species, comprising the steps of:

introducing said feed stream into a vessel, said vessel comprising a wall adapted to define a volume of liquid within said vessel,

cooling said feed stream to produce pressurised LNG within said vessel under conditions of pressure and temperature whereby said at least one said freezable species preferentially forms solids away from said wall of said vessel;

withdrawing said pressurised LNG containing said solids from said vessel; and

separating said solids from said pressurised LNG.

Preferably said step of cooling includes the step of passing said feed stream through an expansion means. More preferably said expansion means is a Joule-Thompson valve.

Preferably said step of withdrawing said LNG containing solids from said cooling vessel is conducted simultaneously with said step of separating said solids from said pressurised LNG. More preferably said process further includes the step of providing said vessel with integral means for solid separation. More preferably still said process further includes means for providing a cyclone integral with said cooing vessel for separating said solids.

Preferably said process further comprises the step of creating a vortex in the volume of liquid within said vessel, said solids preferentially accumulating within said vortex. Preferably said step of creating a vortex comprises stirring said pressurised LNG.

Alternatively said step of creating a vortex comprises the step of introducing a source of sub-cooled LNG through a tangential inlet to said vessel. Preferably said step of introducing a source of sub-cooled LNG further cools said natural gas feed stream.

According to another aspect of the present invention there is provided a vessel for the production of pressurised LNG from a natural gas feed stream containing at least one freezable species, said vessel comprising;

a wall adapted to define a volume of liquid within said vessel, said wall being constructed from a material having a low thermal conductivity,

a first inlet for introducing said feed stream into said cooling vessel;

cooling means for cooling said feed stream to produce pressurised LNG under conditions of pressure and temperature within said vessel whereby said one freezable species forms solids preferentially away from said wall of said vessel; and

an outlet for withdrawing said pressurised LNG containing solids from said vessel.

Preferably said outlet is adapted to separate liquids and solids. More preferably said outlet is a cyclone.

Preferably said first inlet includes an expansion means. More preferably said expansion means is a Joule-Thompson valve.

Preferably said vessel further comprises means for creating a vortex in the volume of liquid within said vessel, said solids preferentially accumulating within said vortex. Preferably said means for creating a vortex comprises a stirring means.

Alternatively said means for creating a vortex comprises a second inlet adapted to be tangential to said vessel for introducing a source of sub-cooled LNG to said vessel.

Preferably said material of construction is sapphire. More preferably said material of construction is single-crystal sapphire. Preferably said material of construction is highly polished.

Brief Description of the Drawings

The present invention will now the described, by way of example only, with reference to the accompanying drawings, in which:

Figure 1 is a schematic diagram representing a process for LNG liquefaction in accordance with a preferred embodiment of the present invention.

Figure 2 is a schematic diagram representing a process for LNG liquefaction in accordance with another embodiment of the present invention including a stirring means within the vessel for creating a vortex and a sub-cooled LNG stream introduced via a second inlet.

Figure 3 is a schematic diagram representing a process of LNG liquefaction in accordance with yet another embodiment of the present invention including a separation means integral with the vessel and a vortex created by the introduction of a sub-cooled LNG stream through a second inlet arranged to be tangential with the vessel.

Detailed Description Of A Preferred Embodiment Of The Invention

The present invention relates to a process and apparatus for the production of pressurised LNG from a natural gas feed stream containing at least one freezable species. Throughout this specification, the term "freezable species" will be understood to include carbon dioxide, water, heavy hydrocarbons and other components that will solidify at the cryogenic conditions usually encountered in an LNG process. A typical natural gas feed stream composition in mol% follows:

Feed gas Composition (mol %):

Methane	70%
Ethane	7%
Propane	3%
i-Butane	0.4%
n-Butane	0.6%
i-Pentane	0.5%
n-Pentane	0.4%

n-Hexane+	0.1%
Nitrogen	3%
Carbon Dioxide	15%
Water	-20^{0}C dew pt.

With reference to Figure 1, a natural gas feed stream 12 including at least one freezable species is introduced into a vessel 10 constructed of a material having a low heat transfer co-efficient. The feed stream 12 is cooled within the vessel 10 to form pressurised liquid natural gas (PLNG) 14 at conditions of temperature and pressure such that the freezable species preferentially form solids away from the wall 11 of the vessel 10. The PLNG containing solids 14 so formed within the vessel 10 is then withdrawn from the vessel via outlet 24. The solids contained within the PLNG must be removed from the PLNG stream by passing the PLNG containing solids through a solids separator 16. The purified PLNG stream 18 is then sent for further cooling and storage. The solids removed be solids separator 16 are discharged via discharge chute 32.

In accordance with a preferred embodiment of the present invention, the natural gas feed stream 12 enters the cooling vessel 10 via an expansion means 20 such as a Joule-Thompson valve or turboexpander. A constant pressure is maintained immediately before the JT valve 20 to ensure controlled expansion of the gas from the high pressure in the inlet pipe 22 to the lower pressure internal to the vessel 10. Testing has shown that the optimum results for liquefaction have been obtained by utilising an inlet gas pressure to the JT valve 20 ranging between 200 to 600 psi. At this range of pressure, gas temperature upstream of the JT valve 20 must not fall below –56°C which is the CO_2 freezing temperature for that pressure range. This process of expansion cools the feed stream 12 entering the vessel 10 to between -100°C to -125°C and reduces the pressure to between 150 and 250 psig.

Optionally, as depicted schematically in Figure 2, the cold gas exiting the JT valve 20 may be further cooled down to –140°C by contacting it with a stream of sub-cooled LNG 26 introduced to the vessel 10 via second inlet 28. In the process, the natural gas

feed stream 12 containing freezable species is further cooled and partially liquefied by direct contact with the sub-cooled LNG 26 thereby causing the freezable species to form solids within the cryogenic PLNG 14. The sub-cooled LNG 26 preferably enters the vessel 10 through a second inlet 28 adapted to be tangential to the vessel 10 and located near the top of the PLNG 14 contained with vessel 10. This arrangement has the result of creating a vortex 30 within the PLNG containing solids 14 within the vessel 10. Due to the density of the solids being greater than that of the PLNG, the effect of the vortex 30 is to draw the solids formed from the freezable species towards the wall 11of the vessel 10. The solids then migrate down the inside body of the vortex 30 and are finally discharged through the outlet 32 from the bottom of the vessel 10. The less dense LNG is drawn to the low pressure rising core of the vortex and removed through a centre discharge line.

The vortex 30 can alternatively be established by mechanical means using a stirring means 34 located towards the bottom of the vessel 10 as depicted in Figure 2.

The two-stage approach (JT expansion and intimate mixing with sub-cooled LNG) maximises the opportunity for freezable solids and in particular CO_2 to solidify. For example, with a feed gas containing 21% CO_2 and at -52°C, in intimate contact with the liquid at about –160°C the majority of the CO_2 will solidify leaving a concentration of approximately 0.2%CO_2 in the PLNG. The formation of ice or hydrates from water in the feed gas and the solidification of heavy hydrocarbons will also take place as part of the process. The resulting mixture of PLNG and solids 14 is withdrawn from the vessel 10 through the outlet 24 at a temperature in the range of -130°C and -150°C and a pressure of between 150 and 250 psig.

According to classic nucleation theory, solids formation is known to occur in the area with the most favourable energetic conditions, ie those conditions which result in the greatest reduction in the overall energy of the system. This is typically the coldest areas of the vessel and/or at a surface. Solidification at a surface requires less surface area per unit volume than the formation of solids independent of a surface. In the absence of

special circumstances, solids will almost always prefer to nucleate at a surface or material defect.

In a conventional liquefaction process using equipment constructed of conventional materials, solids are known to form preferentially on the surfaces of the vessel or heat exchanger baffles which are the coldest part of the main cryogenic vessel. This is partly because in conventional LNG cooling vessels, aluminium and its alloys are used for the walls of the vessel. These materials are known to have a high heat transfer co-efficient among common metals and this has previously been considered essential for efficient heat exchange during the liquefaction process.

In the process and apparatus of the present invention, the vessel 10 and in particular the wall 11 is constructed from a material having a low heat transfer co-efficient in a radical departure from conventional material selection practice. A prototype vessel constructed for testing of the present invention was made from synthetic sapphire. Moreover, the sapphire material of construction was single-crystal sapphire which was highly polished. The single-crystal anisotropic microstructure of the sapphire is believed to serve as a further deterrent to solidification of freezable solids at the walls of the vessel. A polished sapphire surface is ranked among the smoothest known. Without wishing to be bound by theory, it is believed that this property contributes to making the walls of the vessel less energetically favourable for nucleation and precipitation of solids.

It is to be clearly understood that the present invention is not to be limited in scope to the selection of sapphire for construction of the vessel. Any other suitable material having a low heat transfer co-efficient and preferably capable of being polished to a low surface roughness would be equally applicable, for example ceramics such as partially stabilised zirconia or certain high nickel alloys. Using a vessel constructed from a material having a low heat transfer co-efficient, solids formation has been observed in the liquid itself and not on the surfaces in the vessel. The low heat transfer co-efficient of the material of construction has the result that the liquid within the vessel is the coldest part of the vessel.

Without wishing to be bound by theory, the solids formation according to the present invention is believed to rely on two different phenomena; namely, differences in surface tension due to differences in temperature in the cryogenic liquid and differences in density. It is known that liquids at low temperatures have a higher surface tension than those at higher temperatures. A cryogenic liquid held in a vessel constructed from a material having a low heat transfer co-efficient will be colder at the centre than at the vessel wall. The surface tension is thus greatest at the cold centre. This is believed to contribute to solids such as CO_2, solids preferring to segregate and/or precipitate at the colder centre of the vessel. As these solids molecules move towards the cooler centre of the vessel, they are believed to drag the fluid surrounding them. This phenomenon is known as "thermocapilliary flow".

The smooth surface of the vessel, being highly polished sapphire, has no "cold spots", or other irregularities, so this motion takes place uninhibited. In testing, it has been observed that the solids that do precipitate on the walls of the vessel exhibit a planar growth habit and are readily detachable with the motion of fluid due to thermocapilliary flow within the vessel. Should any solids form at and block inlet and/or outlet nozzles, warm dry refrigerant gas can be injected locally to remove any potential build-up of slurry or solids.

During testing, the temperature outside the vessel was around -110^{0}C and inside the vessel was around -120 to -140^{0}C. When the LNG starts to form inside the vessel, the surface tension increased to > 14dynes/cm and the solid micro-crystals were forced away from the warmer regions (vessel walls) towards the cooler regions of higher surface tension at the centre of the vessel.

The solids of the freezable species which begin to form when the natural gas feed stream 12 contacts the sub-cooled LNG spray 26 or the PLNG 14 in the vessel 10 will have a density that is higher than that of the PLNG. These solids need to be separated from the PLNG by using a means for solids separation 16 before it is sent for further processing, cooling and storage. The means for solids separation 16 can be by gravity, cyclone, strainer or other conventional solids separation means. A combination of

gravity and hydro-cyclone methods are preferred. It is however to be clearly understood that it is within the scope of the present invention for the solids separator to comprise s one or more cyclones in series or parallel downstream of the vessel.

In another preferred embodiment of the present invention as depicted in Figure 3, the solids are removed by means of a solids separator 16 integral with the outlet 24 of the vessel 10 through which the PLNG containing solids 14 is withdrawn from the vessel 10. When the solids separator 16 and vessel 10 are integrated, the vessel 10 effectively operates as a form of modified hydrocyclone. The outlet 24 of the vessel 10 then acts as the solids separator 16. Hydro-cyclones employ centrifugal forces many times greater than the simple gravity force to separate solids from a liquid.

Following the removal of solids, the purified PLNG stream 30 may be further cooled to a temperature and pressure suitable for the desired method of transport. The design of the refrigeration system needs to match the process requirements to remove the solids.

It will be readily apparent to a person skilled in the relevant art that the present invention has significant advantages over the prior art including, but not limited to, the following:

a) a low cost liquefaction and refrigeration process which significantly enhances the economics of small scale PLNG production;

(b) small-scale LNG plants based on the process of the present invention become competitive with large-scale projects on a specific capital cost basis ($/tpy) and on a total production cost basis ($/GJ);

(c) A wide variation in feed gas compositions can be processed; and

(d) the process is simpler to operate and maintain than the conventional pretreatment process.

Now that an embodiment of the present invention has been described in detail, it will be apparent to those skilled in the relevant arts that numerous modifications and variations may be made without departing from the basic inventive concepts. While the

technology is particularly intended for use for small-scale LNG production facilities, it is equally applicable to large-scale and offshore LNG production. All such variations and modifications are to be considered within the scope of the present invention, the nature of which is to be determined from the foregoing description.

DATED this 18th day of January 2002

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and
CORE LABORATORIES AUSTRALIA PTY LTD
By Its Patent Attorneys
GRIFFITH HACK

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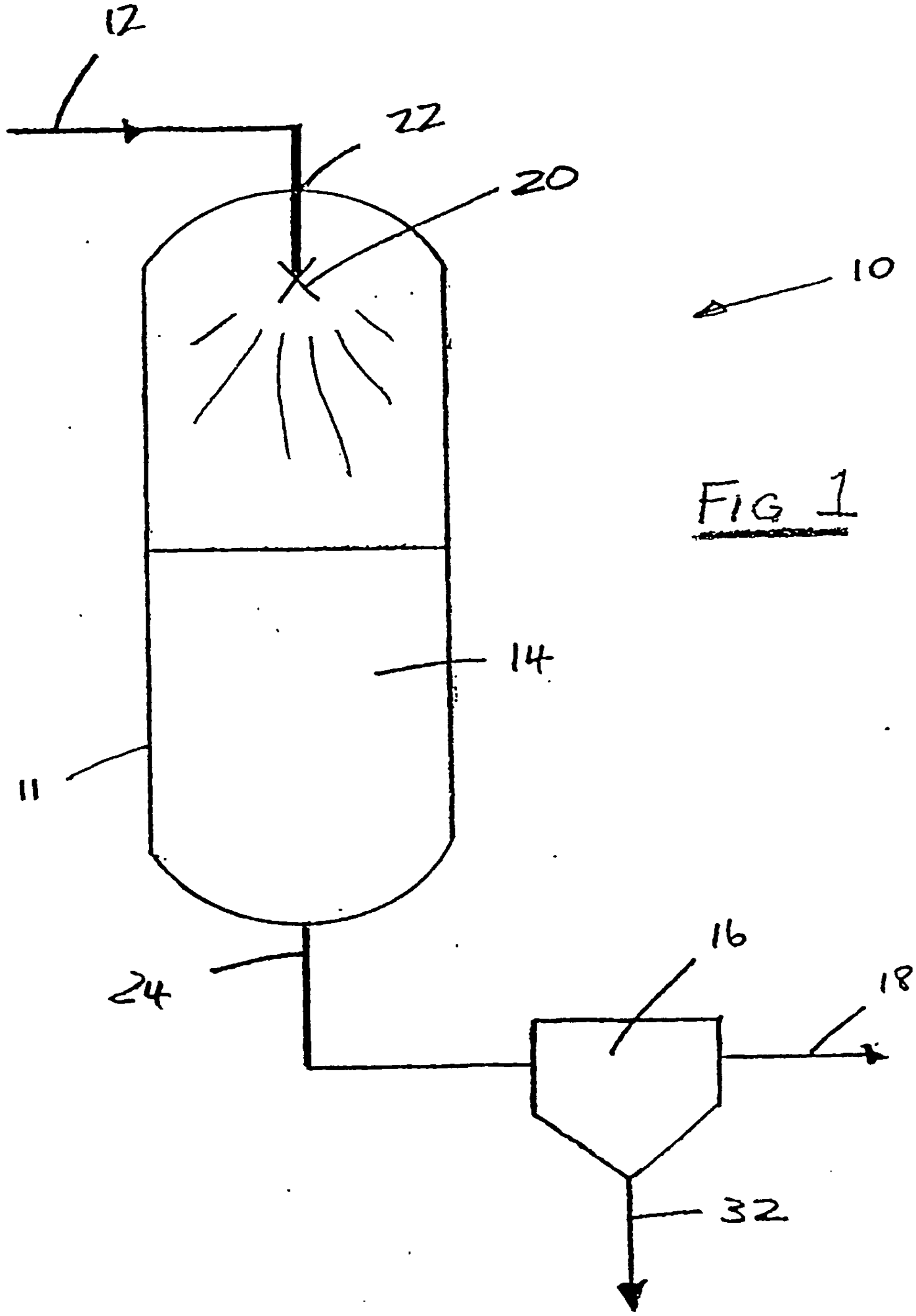

FIG 1

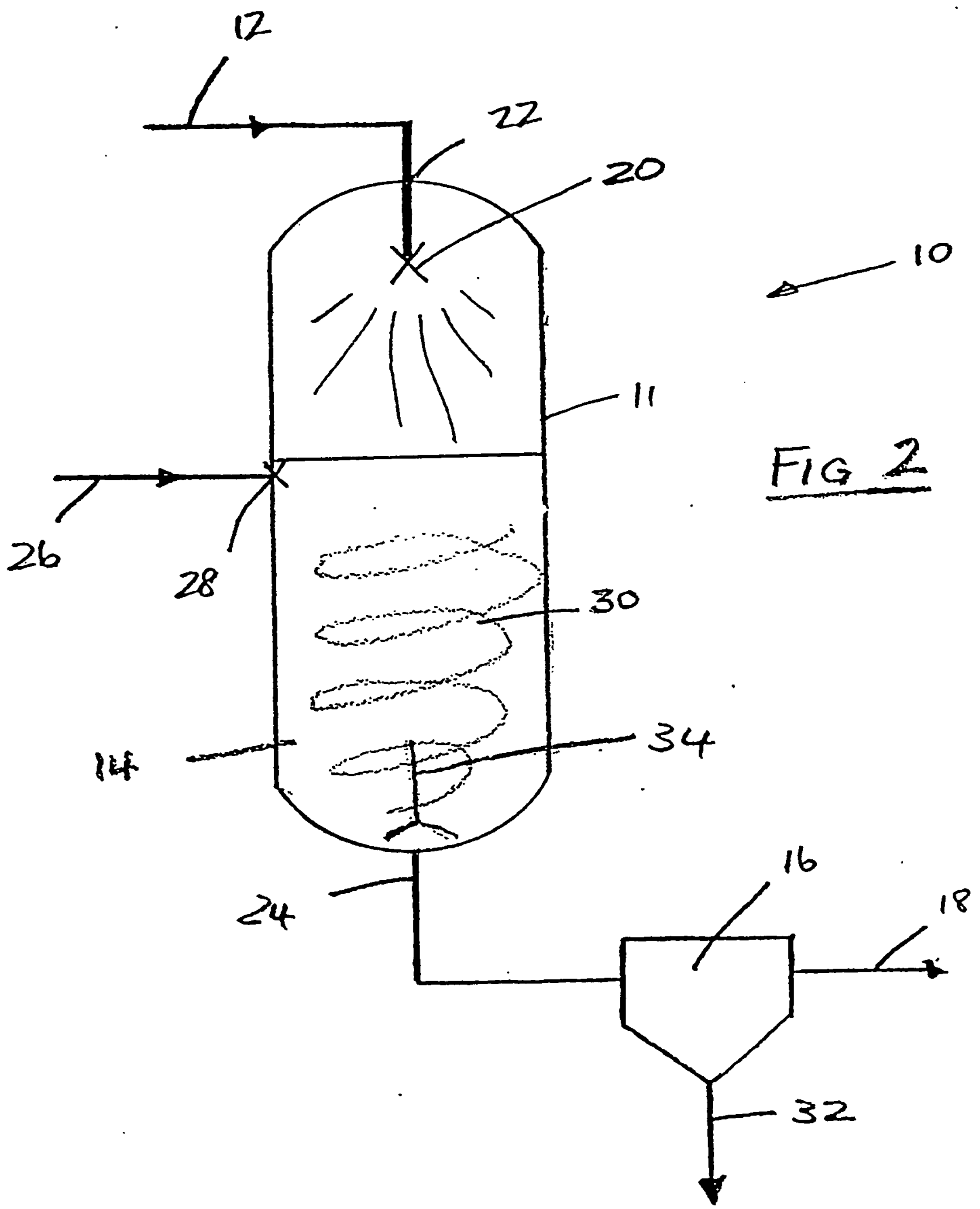

FIG 2

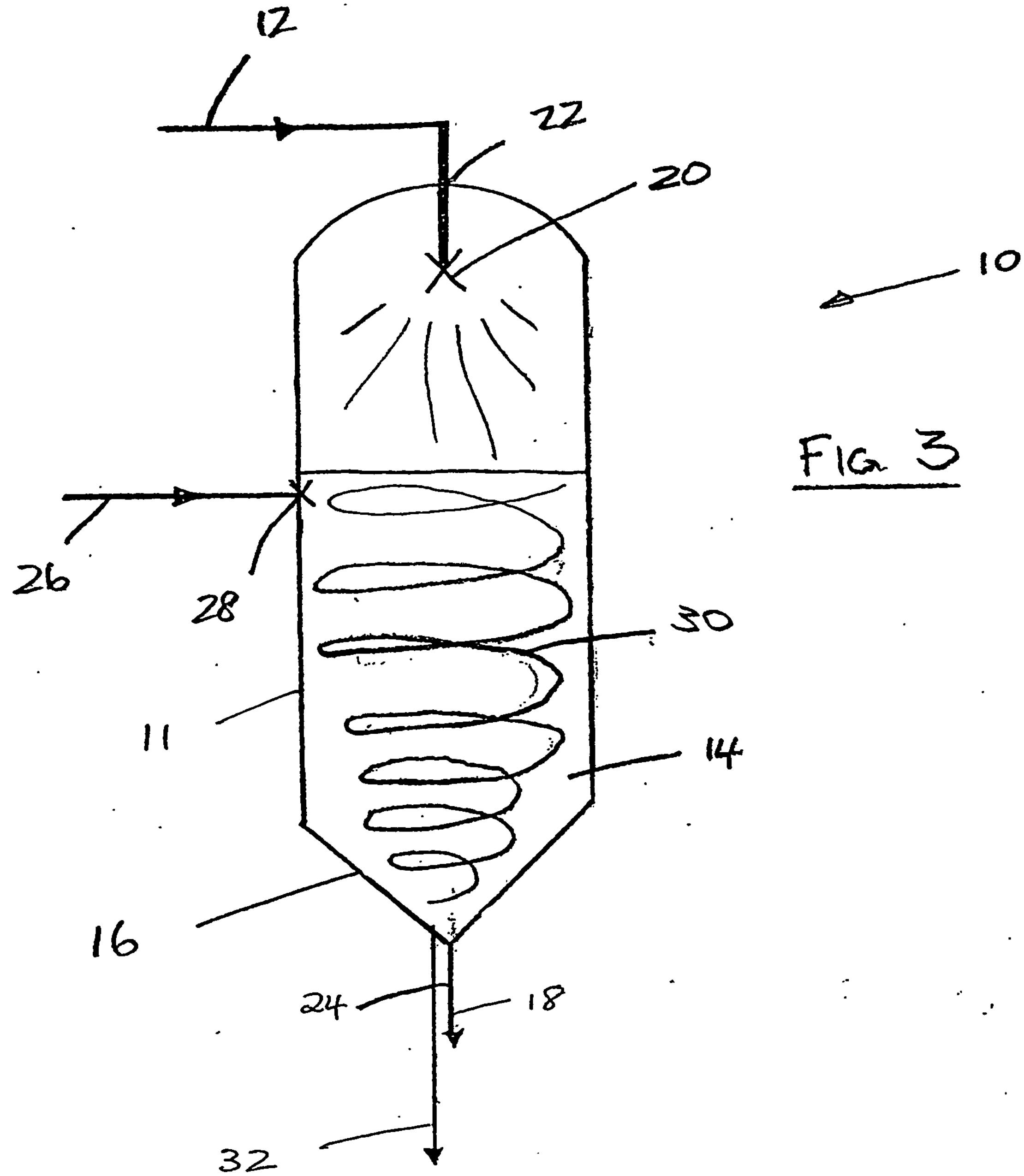

FIG. 3